Reversible Random Sequential Adsorption on a One-Dimensional Lattice

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Abstract

We consider the reversible random sequential adsorption of line segments on a one-dimensional lattice. Line segments of length $l \geq 2$ adsorb on the lattice with a adsorption rate K_a, and leave with a desorption rate K_d. We calculate the coverage fraction, and steady-state jamming limits by a Monte Carlo method. We observe that coverage fraction and jamming limits do not follow mean-field results at the large $K = K_a/K_d >> 1$. Jamming limits decrease when the length of the line segment l increases. However, jamming limits increase monotonically when the parameter K increases. The distribution of two consecutive empty sites is not equivalent to the square of the distribution of isolated empty sites.

INTRODUCTION

The irreversible adsorption of large molecules reported on systems of colloids, proteins, latex spheres, polymer, etc.[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. The most simple model of the irreversible adsorption is the random sequential adsorption(RSA). Large molecules impact sequentially on the surface. If the impacting surface is empty, the molecules adsorb on the surface and do not detach from the surface. If the impacting surface is occupied by molecules, impacting molecules can not adsorb on the surface. Therefore, we expect a formation of a monolayer. In the RSA model the coverage fraction of the surface approaches a limiting value, so called, jamming limit at the long time. In the lattice model of RSA the coverage fraction $\theta(t)$ follows a exponential behavior as $\theta(t) = \theta(\infty) - A\exp(-Bt)$ where $\theta(\infty)$ is a jamming limit, A and B are constants depending on the dimensionality of the surface and the shape of molecules. In the continuous model of RSA or the parking-lot problem, the coverage fraction follows a power-law behavior as $\theta(t) = \theta(\infty) - At^{-\alpha}$ where A is a constant and the exponent α depends on the dimensionality and the shape of the object. The RSA is a oversimplified model for the adsorption of large molecules. Indeed, there are a lot of effects such as the transport of molecules, the diffusion of adsorbed molecules, and the desorption from the surface to the bulk solution[13, 14, 15].

There are many studies on effects of the desorption on the RSA for physical, chemical, and biological systems[1, 2, 3]. A simple example of RSA with desorption is a parking lot problem. Identical cars adsorb(or park) on a line(curb) at the rate K_a. A certain number of parked cars leave a empty space that is too small to fit another car. In the irreversible model of the parking lot (i.e. cars park permanently on the parking lot), the density of cars reaches to the jamming limit $\theta(\infty) = 0.747\cdots$[15]. In the reversible model, the cars park on a line at a rate K_a and leave the line at a rate K_d. In the reversible model the coverage fraction depends on the adsorption and desorption rate. For large values of $K = K_a/K_d$ the coverage fraction shows two different time scales[15, 16, 17, 18]. Jin et.al. studied the adsorption-desorption process of rods on a line. They observed the logarithmic dependence of the coverage fraction[15]. However, their approaches are based on the mean-field idea. Kolan et.al. reported the glassy behavior of the parking-lot model. They observed two different time scales of the coverage fraction by the Monte Carlo method[16]. Ghaskadvi and Dennin reported the reversible RSA of dimers on a triangular lattice[17]. Krapivsky and Ben-Naim

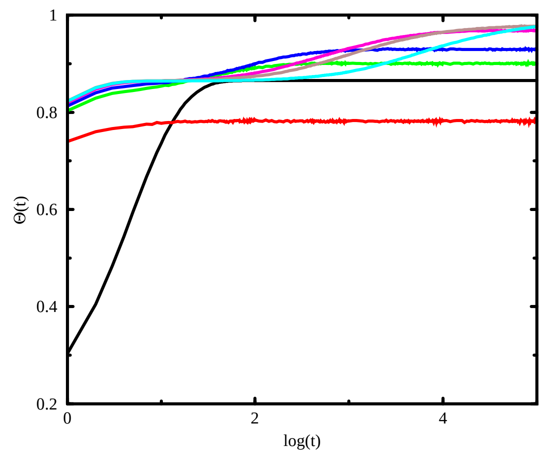

FIG. 1: The coverage fraction $\theta(t)$ versus $\log(t)$ for $l = 2$ with $K = 10, 50, 100, 500, 100, 5000$ from bottom to top, and $K = \infty$(solid line).

reported mean-field results of the coverage fraction for adsorption-desorption processes[18]. They obtained the jamming limit $\theta(\infty) \simeq 1 - 1/\log(K)$, $(K >> 1)$ for the continuum model. The coverage fraction follows a logarithmic dependence such as $\theta(t) \sim 1 - 1/\log(t)$ for the desorption controlled limit ($K_a = \infty, K_d =$finite). In the lattice model the steady-state coverage fraction was given as $\theta_{eq} = 1 - (1/K)^{1/l}/l$ $(K >> 1)$ where l is the length of adsorbed objects.

In this work we consider the reversible RSA process on the one-dimensional lattice by using Monte Carlo simulation. We observed that the coverage fraction shows three time scales for large values of l. However, the jamming limit at the steady-state do not follows the mean-field behavior for the large K. In section II we present the Monte Carlo method of the reversible RSA. We give results and discussions in section III and concluding remarks in section IV.

REVERSIBLE RSA MODEL AND MONTE CARLO METHOD

Consider a one-dimensional clean lattice initially. In the reversible RSA model, a line segment of a length l drops on the lattice at the rate K_a. Adsorbed l-mers are desorbed from the lattice at the rate K_d. We select randomly a lattice site. If the selected site is empty, we try to adsorb a line segment of length l with a probability $p_a = K_a/(K_a + K_d)$. We generate a random number $p(0 < p \leq 1)$. If $p < p_a$, we try to drop a line segment on

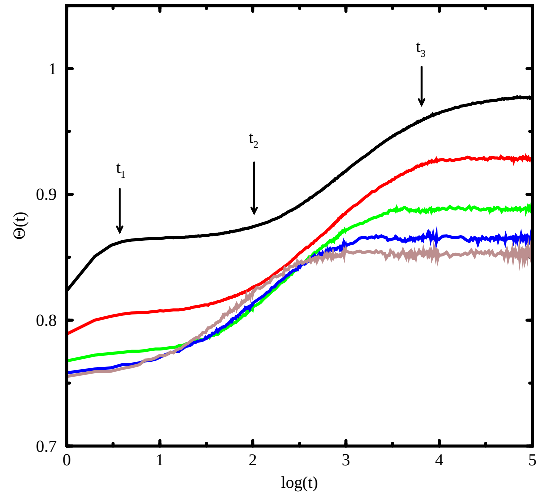

FIG. 2: The coverage fraction $\theta(t)$ versus $\log(t)$ for $K = 1000$ with $l = 2, 4, 8, 16, 32$ from top to bottom.

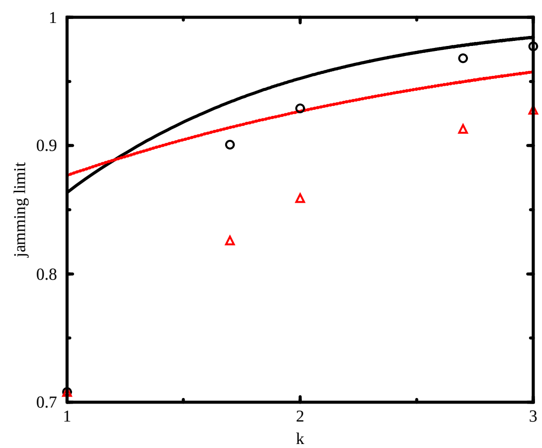

FIG. 3: The steady state jamming limit against the parameter $\log(K)$ for $l = 2(\circ)$ and $l = 4(\triangle)$. Solid lines represent mean field results.

the lattice. In the trial of adsorption we check $(l-1)$ consecutive neighbors. If l-consecutive lattice sites are all empty, l-mers adsorb on the lattice. Otherwise, the trial is rejected and increase a Monte Carlo step. If the selected site is occupied by the adsorbed line segment, we generate a random number p. If $p > p_a$, the occupied line segment desorbs from the lattice. Otherwise, the trial of desorption is rejected and increase a Monte Carlo step.

It is not allowed to adsorb a line segment on occupied sites. So we expect a formation of the monolayer. Kinetics of the coverage fraction is controlled by a parameter $K = K_a/K_d$.

We set $K_d = 1$ and control the adsorption rate K_a. So that, a line segment will be desorbed from the lattice every $(K_a + K_d)$-trials.

We consider a lattice of size $L = 10^4$ with a periodic boundary condition. The lattice is a one-dimensional ring with a length L. We also check the finite size effect for the large lattice with $L = 10^5$. We calculate the coverage fraction as a function of the time. The coverage fraction was averaged over 100 different configurations. One Monte Carlo time corresponds to L adsorption/desorption trials regardless of successful or unsuccessful trials. Maximum Monte Carlo times were up to $t = 10^5$.

RESULTS AND DISCUSSIONS

Consider the reversible RSA process of the line segment with the length $l = 2$. In Fig. 1 we present the coverage fraction versus the time. For the irreversible RSA ($K = \infty$), the coverage fraction saturates exponentially to a jamming limit $\theta(\infty) = 0.868\cdots$. For a small K (for example $K = 10$) the jamming limit at the steady-state is smaller than that of the irreversible RSA. When the parameter K increases we observed two different linear regions of the coverage fraction when we plot the coverage fraction $\theta(t)$ against $\log(t)$. The coverage fraction increases rapidly at the early times $t < t_1$, and converges to the jamming coverage fraction of the irreversible RSA at $t_1 < t < t_2$ as shown in Fig. 2. In the former region the adsorption controls the kinetics of the RSA. The time t_1 and t_2 increase when the length of the line segment l increases as shown in Fig. 2. At $t_2 < t < t_3$ the coverage fraction increases linearly up to the saturation time t_3 when we plot the coverage fraction $\theta(t)$ against $\log(t)$. In this region the coverage fraction is proportional to $\theta(t) \sim \log(t)$. At $t > t_3$ the coverage fraction saturates to the steady-state jamming limit. Steady-state jamming values increase when the parameter K increases.

In Fig. 2 we gave the coverage fraction $\theta(t)$ versus $\log(t)$ for a fixed $K = 1,000$ and the different length of the line segment l. When the length of the line segment increases, we observe clear four stage behaviors of the coverage fraction. For small values of the line segment $l < 8$, the time t_1 is very small and the coverage fraction approaches to the irreversible jamming value rapidly. The times t_2 and t_3 increase as the length of the line segment increase. Steady-state jamming values decreases when the length of the line segment l increases.

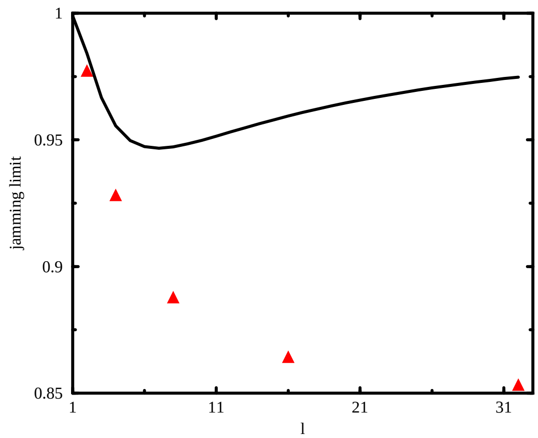

FIG. 4: The steady state jamming limit against the length of the line segment l for $K = 1000$. The solid line represent the mean field result.

In Fig. 3 we present the stead-state jamming limit versus the parameter K for $l = 2(\circ)$ and $l = 4(\square)$. The solid line is the mean-field prediction $\theta(\infty) = 1 - (1/K)^{1/l}/l$ for $K >> 1$[18]. Steady-state jamming limits are not coincident with mean-field predictions. Monte Carlo results are always smaller than those of mean-field results. Steady-state jamming limits increases monotonically when the parameter K increases.

In Fig. 4 we show steady-state jamming limits against the length l of line segments. Jamming limits decrease monotonically when the length l increases. Mean-field results of jamming limits (solid lines in Fig. 4) have a minimum point. However, our Monte Carlo results do not have a minimum point of the jamming limit. The non-mean field behavior of steady-state jamming limits can be understood by the empty site distribution.

In Fig. 5 we represent the number of empty sites; the total number of empty sites $N(t)$, the number of isolated single empty sites $N(x0x, t)$, the number of two consecutive empty sites $N(x00x, t)$, the number of isolated empty sites separated by $l = 2$ occupied sites $N(x0xx0x, t)$, and the number of an isolated empty site and two consecutive empty sites separated by $l = 2$ occupied sites $N(x0xx00x, t)$ where x means an occupied site and 0 denotes an empty site. The total number of empty sites $N(t) = (1 - \theta(t))L$ saturates to steady-state limits at long times as shown in Fig. 5 (a) and (c). The early time behavior of the empty site is controlled by collective behaviors of the single empty site, double empty sites, and higher empty sites. The number of two consecutive empty sites $N(x00x, t)$ shows

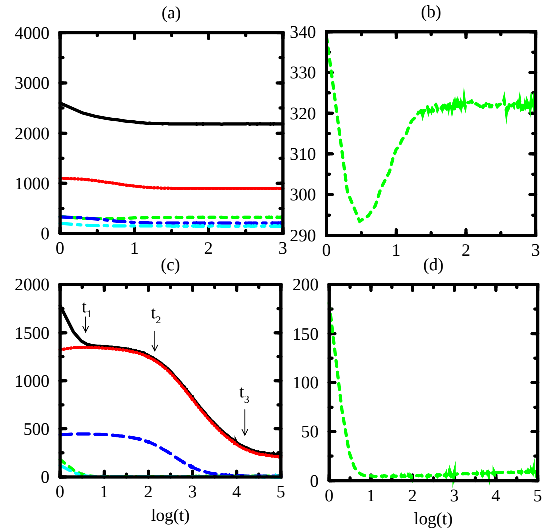

FIG. 5: The time dependence of empty site distributions with $l = 2$. We present different kinds of empty site distributions, the total number of empty sites $N(t)$(solid line), the number of an isolated empty site $N(x0x, t)$(dotted line), the number of consecutive two isolated empty sites $N(x00x, t)$(dashed line), the number of two isolated empty sites separated by $l = 2$ occupied sites $N(x0xx0x, t)$(longdashed line), and the number of an isolated empty site and two consecutive isolated sites separated by $l = 2$ occupied sites $N(x0xx00x, t)$(dotdashed line) (a) for $K = 10$, (c) for $K = 1000$. Short time behaviors of $N(x0xx00x, t)$ (b) for $K = 10$ and (d) for $K = 1000$.

a minimum point around the time t_1 and saturates to a steady-state value at $t > t_1$ as shown in Fig. 5 (b) and (d). In particular, we observe that $N(x0xx0x, t) \neq N(x0x, t)N(x0x, t)$ and $N(x0xx00x, t) \neq N(x0x, t)N(x00x, t)$. The mean-field prediction is based on the approximation $N(x0xx0x, t) = N(x0x, t)^2$ and $N(x0xx00x, t) = N(x0x, t)N(x00x, t)$. We conclude that the coverage fraction of the reversible RSA can not explain by the mean-field approximation because there is strong collective behaviors of empty site distributions. For large K(for example $K = 1000$) the total number of empty sites $N(t)$ are controlled by $N(x0xx0x, t)$ at the early time $t < t_1$.

In Fig. 5 (c) we also observe typical four stages of the coverage fraction. At $t < t_1$ the coverage fraction increases due to the dominant process of the adsorption. At $t_1 < t < t_2$ the coverage fraction saturates to the jamming limit of the irreversible RSA. In these region $N(x0x, t)$ and $N(x0xx0x, t)$ decays slowly up to time t_2 as shown in Fig. 5 (c). At $t_2 < t < t_3$ the coverage fraction increases as $\theta(t) \sim \log(t)$ and $N(t) \sim (\log t)^{-1}$. In this region isolated

single empty sites $N(x0x,t)$ and $N(x0xx0x,t)$ decrease logarithmically, while $N(x00x,t)$ decreases very slowly and saturates to a steady-state value. At $t > t_3$ empty sites distribution converges to a limiting value and the empty sites strongly depend on isolated empty sites at $t > t_3$.

CONCLUSIONS

We have observed that the coverage fraction of the reversible RSA does not show the mean-field behavior on the one-dimensional lattice. Jamming limits of the coverage fraction decrease monotonically for the length of the line segment l. The distribution of two consecutive empty sites is not production of the distribution of isolated single empty sites.

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[1] V. Privman, Trends Stat. Phys. **1**, 89(1994).

[2] V. Privman, *Nonequilibrium Statistical Mechanics in One Dimension* (Cambridge Univ. Press, Cambridge 1997).

[3] J. W. Evans, Rev. Mod. Phys. **65**, 1281(1993).

[4] P. J. Flory, J. Am. Chem. Soc. **61**, 1518(1939).

[5] E. R. Gonzalez, P. C. Hemmer, and J. S. Hoyer, Chem. Phys. **3**, 228(1974).

[6] J. Feder, and Giaver, J. Colloid Int. Sci. **78**, 144(1980).

[7] G. Y. Onoda, and E. G. Liniger, Phys. Rev. A **33**, 715(1986).

[8] J. J. Ramsden, Phys. Rev. Lett. **71**, 295(1993).

[9] J. W. Lee, J. Phys. A**29**, 33(1996).

[10] J. W. Lee, Phys. Rev. E **55**, 3731(1997).

[11] J. W. Lee, and B. H. Hong, J. Chem. Phys. **119**, 533(2003).

[12] V. Privman, H. L. Frisch, N. Ryde, and E. Matijvec, J. Chem. Soc. Faraday Tranc. **87**, 1371(1991).

[13] N. -H. L. Wang, AIChE J. **40**, 1685(1994).

[14] P. Schaaf, J. -C. Voegel, B. Senger, Ann. Phys. Fr. **23**, 1(1998).

[15] X. Jin, G. Tarjurs, J. Phys. A**27**, L195(1994).

[16] A. J. Kolan, E. R. Nowak, and A. V. Tkachenko, Phys. Rev. E **59**, 3094(1999).

[17] R. S. Ghaskadvi, and M. Dennin, Phys. Rev. E **61**, 1232(2000).

[18] P. L. Krapivsky and E. Ben-Naim, J. Chem. Phys. **100** 6778(1994).